MOULTON

The Combustion of
Organic Substance
by use of Sodium Per-Oxide

Chemical Engineering

B. S.

1907

THE COMBUSTION

OF

ORGANIC SUBSTANCE,
BY USE OF SODIUM PER-OXIDE

BY

CHARLES ROBERT MOULTON

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

PRESENTED JUNE, 1907

UNIVERSITY OF ILLINOIS

May 31   190 7.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY
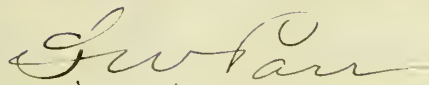
Charles Robert Moulton

ENTITLED The Combustion of Organic Substance, by Use of Sodium

Per-Oxide.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF   Bachelor of Science

in Chemical Engineering.

S. W. Parr

Instructor in Charge.

APPROVED: *S. W. Parr*

HEAD OF DEPARTMENT OF *Chemistry*.

THE COMBUSTION OF ORGANIC SUBSTANCES BY USE OF SODIUM PEROXIDE.

Previous to 1886 the production of cheap and pure metallic sodium and sodium peroxide was still a problem of the future. Consequently the extensive use of either as a reagent was practically prohibited. But in 1886 with the perfecting of Castner's process for manufacturing metallic sodium its abundance and cheap production was assured. As sodium peroxide is obtained most cheaply and purely by direct heating of the metallic sodium it can be seen what an increase in the use of the peroxide was now made possible by its cheapness.

Investigations soon were undertaken to determine the applications of the peroxide. Thus it has been within the last decade and a half that sodium peroxide has come into prominent use as a fusion or combustion medium for organic and inorganic substances intended to be analyzed. The earliest work, perhaps, on its use as an analytical agent was published by John Clark[1] in 1893. Previously[2] in 1871 he had pointed out the strong oxidizing action of a mixture of caustic soda and calcined magnesia when used in the estimation of chromium. He was now certain, however, that this oxidizing action was due to the formation of the peroxides of sodium and magnesium, for both

had been detected by him in the soluble and insoluble portions of the fusion.

About the same time Walter Hempel[3] had pointed out the superiority of sodium peroxide over other oxidizing agents. He has shown that as an oxidation reagent with the use of heat it takes a place ahead of all other reagents on account of both its purity and the rapidity of its action, and in spite of its quick, sudden action it can be easily employed without danger or loss. It is excellent for the detection of chromium and manganese and for rendering titanium ore soluble, but he considers that for the oxidation of sulphur compounds it is absolutely necessary to reduce the violence of its action by the addition of sodium carbonate. He states that half and half gives good fusions with pyrites, galena, and zinc blende.

Clark endorses Hempel's remarks but he prefers sodium peroxide without the carbonate. For pyrites he recommends six times the weight of peroxide in a platinum or nickel crucible. The sulphur is determined in the water solution. It is his observation that owing to the suddenness of its oxidation sodium peroxide cannot be heated with coal or coke, even when mixed with sodium carbonate, without a violent deflagration. In contact with combustible matter it gives off its action at

so low a temperature that it is dangerous to keep it in paper

for the heat of the hand is sufficient to set it off.

In 1895 Albert Edinger[4] published a series of experiments

to establish the fact that one could use sodium peroxide in the

case of a majority of inorganic sulphur compounds to obtain

sodium sulphate and that chlorine as well as sulphur, by the

change to sodium chloride and sodium sulphate, could be easily

determined quantitatively. Edinger pointed out the unsatisfactori-

ness of the Carius method for sulphur because of the impurity

(barium nitrate) that was formed along with the sulphate on account

of the use of soda and saltpeter in the tube. He would substitute

the use of sodium or barium peroxyd for the soda and saltpeter

of the above method. For organic chlorine and sulphur compounds

Edinger recommends a water solution of sodium peroxide as well as

sodium peroxide in the dry way by fusion. A number of quantitative

analyses back up his recommendation of the general use of sodium

peroxide for the analysis of inorganic and organic sulphur and

chlorine compounds. Edinger says a mixture of sodium peroxide

and carbonate may be used as well as the simple peroxide and

either a porcelain or platinum crucible.

Poleck[5], Höuel, and Kassner turned their attention

to the action of sodium peroxide on iodine, lead oxide, uranium,

chromium, potassium ferricyanide, and the precious metals.

Kassner[6]worked out a good separation of arsenic, antimony, and
tin. Spüller and Kallman[7] have given a determination of sulphur
instead and pig iron by means of sodium peroxide. In 1894
Hoehnel and Glaser[8] made revised recommendations for the estima-
tion of sulphur in pyrites. In 1896 Schuyler[9] proposed to
determine mercury in mercuric salts by the reduction to the metal
with sodium peroxide.

An application of sodium peroxide in a wet way to
qualitative analytical chemistry was published by S. W. Parr[10]
in 1897. He wrote that "sodium peroxide as a reagent has
properties of a very unusual and striking character. These
properties are no less valuable than peculiar, and indicate
for this substance a prominent place in analytical analysis.
By this means its numerous characteristics can be best illustrated."
In this article Parr outlines a good practical method for the
qualitative analysis of the metals of the third group sodium
peroxide being used as the precipitant in the acidulated
solution. The method has been used in the chemical laboratory
of the University of Illinois with entire satisfaction, thus
abundant by demonstrating the value of the processes involved.
A method of distinguishing between carbon dioxide and sulphur
dioxide when both are present as acids is also given.

In 1898 C. Glaser[11] reported a method which had been

used by him in a considerable number of coal, coke, and asphalt
analyses for sulphur with perfect success. A silver or nickel
dish was used and four times the weight of Na_2CO_3 and a piece of
NaOH one half the weight of the carbonate was placed on top,
the substance to be analyzed being mixed with the carbonate.
A low flame is placed under the dish until the mass is half
fused then dry sodium peroxide is sprinkled on till all the
carbon is burned away.

F.C. Koch[12] in his bachelor's thesis of 1899 entitled
'The Oxidation of Nitrogen' worked with the oxidation of various
nitrogen compounds by the action of sodium peroxide. His
conclusions are that:

1) Free nitrogen is not oxidized by sodium peroxide
in the fused condition.

2) Gaseous ammonia is readily oxidized by fused
peroxide of sodium.

3) Aqueous ammonia is not oxidized by the peroxide.

4) Ammonium sulphide gives no oxidation of the
peroxide.

5) Sodium peroxide acting on ammonium salts may oxidize
up to twenty four per cent of the nitrogen.

6) Potassium cyanide is oxidized by the peroxide,
but an excess of the cyanide again decomposes the oxidation

products.

7) Ammonium sulphocyanate is not oxidized.

8) Urea is partially oxidized and some ammonia is liberated.

9) Magnesium nitride and sodium peroxide give no oxidation where simply heated, but with hot water and the peroxide a slight amount of nitride is formed.

In 1896, while experimenting with the Lewis Thompson Calorimeter, Professor S. W. Parr tried the effect of a small amount of sodium peroxide in the mixture of $KClO_3$ and KNO_3 ordinarily used in this calorimeter. More perfect combustions were obtained, and a more uniform increase of calorific value was found. Naturally the suggestion resulting from these experiments was the possibility of using the sodium peroxide alone, and utilizing its absorptive powers for both water and carbon dioxide. These experiments were continued through 1897, 1898, amd 1899, and the ultimate result from this work is the well known Parr Calorimeter. (See Plates II and III.) Pages 16 + 17.

An important step forward in the use of sodium peroxide was accomplished in 1900 when S. W. Parr[13] came forward with his new coal calorimeter. In his paper he gave the advantages of his new form of calorimeter over the Thompson calorimeter and compared it favorably with the Berthelot and Mahler bombs.

The principle involved in his process depends upon the liberation

of oxygen from such a compound or chemical as shall in turn

absorb the products of combustion thereby avoiding the necessity

of providing conduits for the gases. A chemical which admirably

meets these requirements is sodium peroxide, and so the Parr

Peroxide Calorimeter was perfected. He obtained good calorimetric

results with the Pennsylvania and Illinois coals. Good combustions,

however, were limited to soft bituminous coals. To correct this

failing there was tried fine grinding of the coal to be tested

and the addition of an accelerator in the form of a definite

amount of a standard bituminous coal. No great success was

attendent upon these trials.

In an early number of the Journal of the American

Chemical Society for 1902 S. W. Parr[14] gave the results obtained

in the Zurich Laboratory of the application of the peroxide

calorimeter to anthracite European coals and petroleum. In

place of bituminous coal as an accelerator tartaric acid and

potassium per-sulphate were used. It was found that with 0.5

gram of coal 0.5 gram of tartaric acid with 1 gram of potassium

persulphate and ten or twelve grams of sodium peroxide gave good

results. The ratio of peroxide to coal is twenty to one.

The tartaric acid-persulphate mixture, however, deteriorated

somewhat on standing.

Considerable work has been done in the Chemical Laboratory of the University of Illinois with calorimetric constants and heat correction factors for chemicals under the direction of S. W. Parr. In 1902 Reuben Nelson Kofoid[15] took up a "Study of Calorimetric Methods Together with a Critical Study of the Peroxide Calorimeter." He further investigated the tartaric acid-persulphate mixture above referred to when used with different grades of coal and with naphthalene, starch, benzoic acid, cane sugar, and sugar carbon, and he found that very satisfactory results could be obtained and that the mixture was pretty constant in its action as an accelerator.

In 1903 Hans H. Pringsheim[16] published a method for the rapid estimation of chlorine, bromine, and iodine in organic compounds by means of sodium peroxide. The substance was mixed with sixteen to eighteen times its weight of sodium peroxide and ignited in a covered iron crucible by dropping a hot wire through a hole in the cover. The product was dissolved in water, acidified with nitric acid, and precipitated with silver nitrate. It will be noticed that Pringsheims ratio of eighteen parts sodium peroxide to one part of organic matter is practically the same ratio proposed by S. W. Parr[14] in 1902. The principles in Pringsheim's work are about identical with the principles involved in the application of Parr's Peroxide Calorimeter.

In the year following Fritz von Konek[17] developed a

method for the analysis of carbon, nitrogen, sulphur, phosphorus,
and halogen compounds by the use of peroxide of sodium. Into
a strong, cylindrical nickel, or steel, crucible fitted with
a perforated lid through which passes a ten centimeter long
lickel or steel tube, are introduced five to ten grams of sodium
peroxide and a pinch of the finely powdered sample is added and
the two are mixed by means of an iron wire. When dealing with
volatile compounds which must be tested for nitrogen, and so
forth, a little of a compound rich in carbon, such as camphor,
should be added. The lid is clamped on and the crucible is
placed in a basin of cold water and the mass is ignited by
dropping a red hot iron wire into the hole. A violent reaction
results, and the mass contains carbon as carbon dioxide, nitrogen
as nitrate, sulphur as a sulphate, phosphorus as the orthophosphate,
and halogens as oxygen compounds. Again in von Konek's work
we notice a striking likeness in principle to Parr's work.

In later articles[18] von Konek amplified the above
method for the estimation of organic carbon by means of sodium
peroxide. As to the estimation of organic nitrogen[19] by means
of sodium peroxide he said that, although organic substances are
not as a rule quantitatively converted to nitric acid by
peroxide of sodium, this method gives good results when applied
to the estimation of nitrogen in flour. Flour dried at 100° to

102° C. is mixed in a steel cylinder with an excess of dry sodium

peroxide to which a mixture of potassium persulphate and tartaric

acid had been added. (See Parr's work of 1902[14] for the origin

of this idea.) The cylinder is kept in cool water and when the

vigorous oxidation which is started by a red hot iron wire

introduced into the cylinder is complete the whole mass is

dissolved in water and the nitrate is determined.

In the latter part of this same year, 1904, H. H.

Pringsheim[20] replied to von Konek that as regards nitrogen

up to ninety per cent of it may be liberated as nitrogen

during the reaction with sodium peroxide. He would therefore

discount von Konek's method for nitrogen. Of interest in

connection with this controversy, perhaps, is the work of Koch[12]

done on the oxidation of nitrogen above referred to.

In the Berichte[21] Pringsheim published an article

on the use of sodium peroxide in the qualitative analysis of

organic substances. He said that the ignition of organic

substances with sodium peroxide might be employed for the rapid

and simultaneous qualitative detection of halogens, phosphorus,

arsenic, and sulphur. A mixture of sodium peroxide with one

twenty fifth part of an organic non-hygro-scopic substance,

as napthalene or cannamic acid, is prepared and stored.

Substances to be tested are added to a small quantity of this

mixture in an iron vessel and heated until reaction occurs.
The mass is dissolved in water and the elements tested for in
the usual manner.

In the American Chemical Journal of the same year[22]
Pringsheim goes over the above determination and adds that
substances with seventy five per cent of carbon and hydrogen
need eighteen times their weight of sodium peroxide, those with
fifty to seventy five per cent need sixteen times; twenty
to fifty per cent need one half the weight of sugar as well as
the peroxide, and below twenty-five per cent need the same
treatment as given to below fifty per cent. Pringsheim claims[23]
that the speed, neatness, and safety of the use of sodium peroxide
is undisputed, that it is cheaper and easier to handle than the
Carius tubes, and that it gives very good results for the
determination of halogens, etc., in organic compounds.

In the above work the fusions with sodium peroxide
for the analysis of organic material had,with the exception of
Parr's work with the peroxide calorimeter and von Konek's
work with the crucible and clamped on lid, been carried on in
open vessels or loosely closed crucibles. As a consequence

the methods were limited to use in cases where the reaction was
not violent and no great deflagration took place. All that
has been said above regarding the use of sodium peroxide as a
fusion medium for organic substances in open vessels applies
equally well to the combustion in the peroxide bomb. But the
closed bomb has a great advantage over the open crucible in that
a violent reaction and deflagration may take place in the bomb
without any loss of material and vitiation of the analytical
results to be obtained from the fusion. Thus the closed bomb
greatly enlarges the field of application of sodium peroxide
fusions to qualitative and quantitative analysis. On account
of the ability of the bomb to withstand pressure on the inside
a very quiet combustion may be obtained when an open crucible
would give a violent deflagration or an explosion. Also under
pressure in most cases the tendency to boil up is entirely
removed and a very quiet fusion takes place. Submerging
the peroxide bomb in water while the combustion is going on
allows of a very intense local heat in the bottom of the bomb
without any danger of injury to the material of the bomb. Thus
the need for an expensive platinum lining or porcelain lining
is entirely done away with. The intense local heat causes very
refractory materials to combust with the peroxide.

In 1906 in a thesis entitled: "A Determination and

Study of the Mineral Constituents of Flesh,' Frederic Williams

Gill[24] used the Parr Bomb Calorimeter[13] for the combustion of

air-dried meat. He obtained a good combustion with one gram of

meat, two grams of mixture (eight parts KNO_3 and two parts $KClO_3$),

ten grams of Na_2O_2, and a little NH_4Cl. But the sample of meat

used was too small from which to determine the sulphur, owing

to the small amount of sulphur present. Therefore unless a larger

cartridge could be used this method was not satisfactory for

the determination of sulphur. The method used by Gill for

sulphur was the Osborne Method[25] for sulphur in protein bodies.

An outline of the method follows. Ten grams of Na_2O_2 are

converted into the hydroxide in a nickel crucible by adding a little

water and boiling over an alcohol lamp to expel the excess of

water. One to two grams of protein are stirred into the slightly

cooled hydroxide and oxidized by raising the heat andadding

small portions of Na_2O_2 till the oxidation is complete. The

sulphur is determined in the water solution of the mass.

Considerable work in perfection accelerator mixtures

was done under the direction of S. W. Parr in the laboratory of

the University of Illinois by Ellis B. Hall[26] in his thesis

on 'A Study of Mixtures Available for Combustions with Sodium

Peroxide.' There were many objections to the previous accelerator

mixtures; so Hall worked for an ideal accelerator. Twenty

nine different mixtures were used with $KClO_3$, KNO_3, or NH_4NO_3

as the oxidizer and NH_4Cl, $(NH_4)_2PO_4$, Mg, Al, $B(OH)_3$, or SiO_2

as the heat producers. Good results were obtained with two

parts boric acid to one part KNO_3 and with ten parts boric acid

and four parts $KClO_3$ and one part magnesium. But $KClO_3$

alone was found best in spite of its great activity as an

oxidizing agent and its explosive nature, which entirely disappears

under the conditions existing in the bomb. One and a half

to two grams of $KClO_3$ for cokes, oils, and naphthalene gave good

results. For one half gram of coke one gram and a half of

$KClO3$ was used. For one half gram of bituminous coal one half

gram of $KClO_3$. Potassium chlorate has the advantages as an

accelerator of being a simple, non-hygroscopic compound, remaining

in a fine condition when once ground, of retaining all its

power even on long standing, of containing neither carbon nor

sulphur to interfere in any determination of these constituents
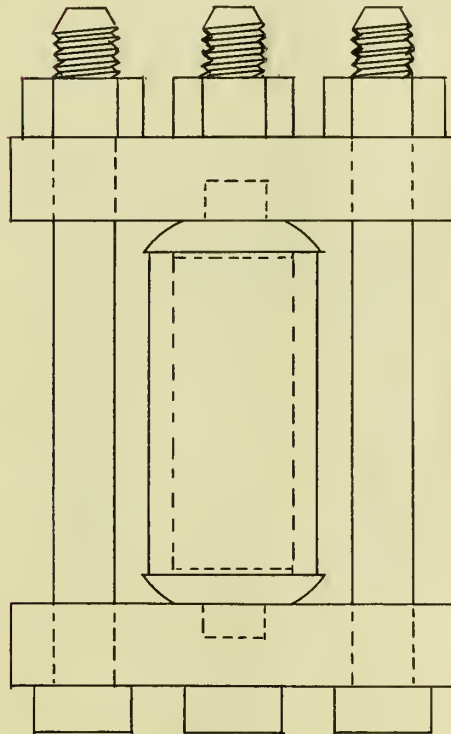
in organic substances, and of being a common, inexpensive

chemical.
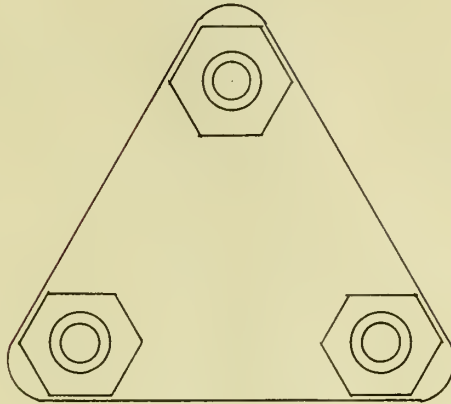
Plate I

Inside Dimensions of Cylinder

$3\frac{1}{2}" \times 1\frac{1}{4}"$

Scale : $6" = 1'$.

BOMB, IGNITION BY EXTERNAL FLAME

May 23, 1907.   C. R. moulton.

Plate II
LARGE
ELECTRIC
IGNITION
BOMB
Scale: 12" = 1'.
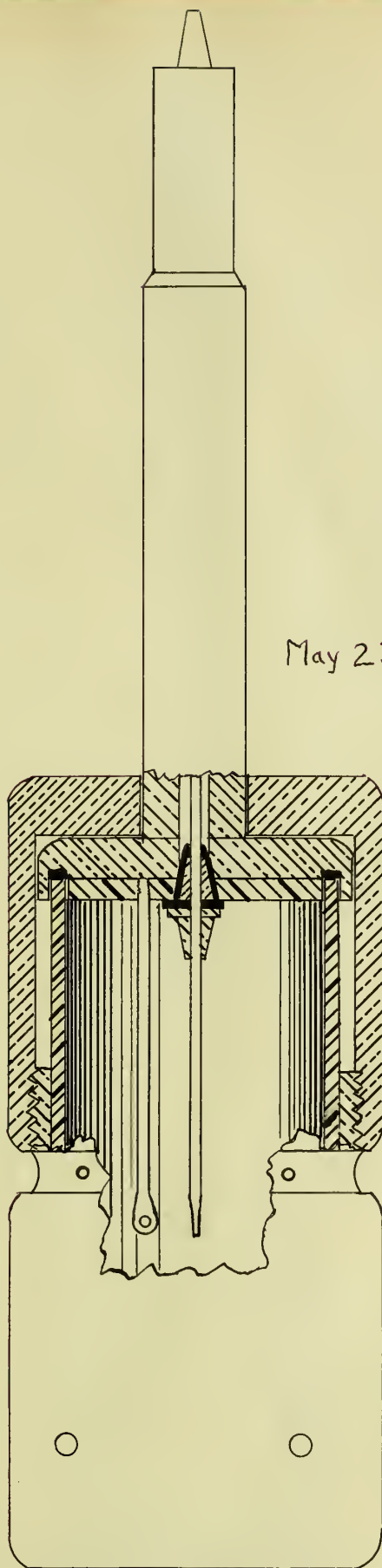May 23, '07.   C.R. Moulton

Plate III
STANDARD
NICKEL STEEL
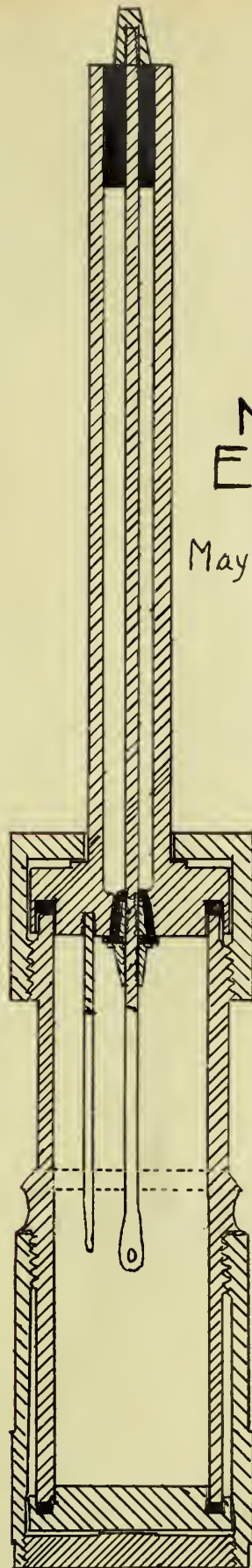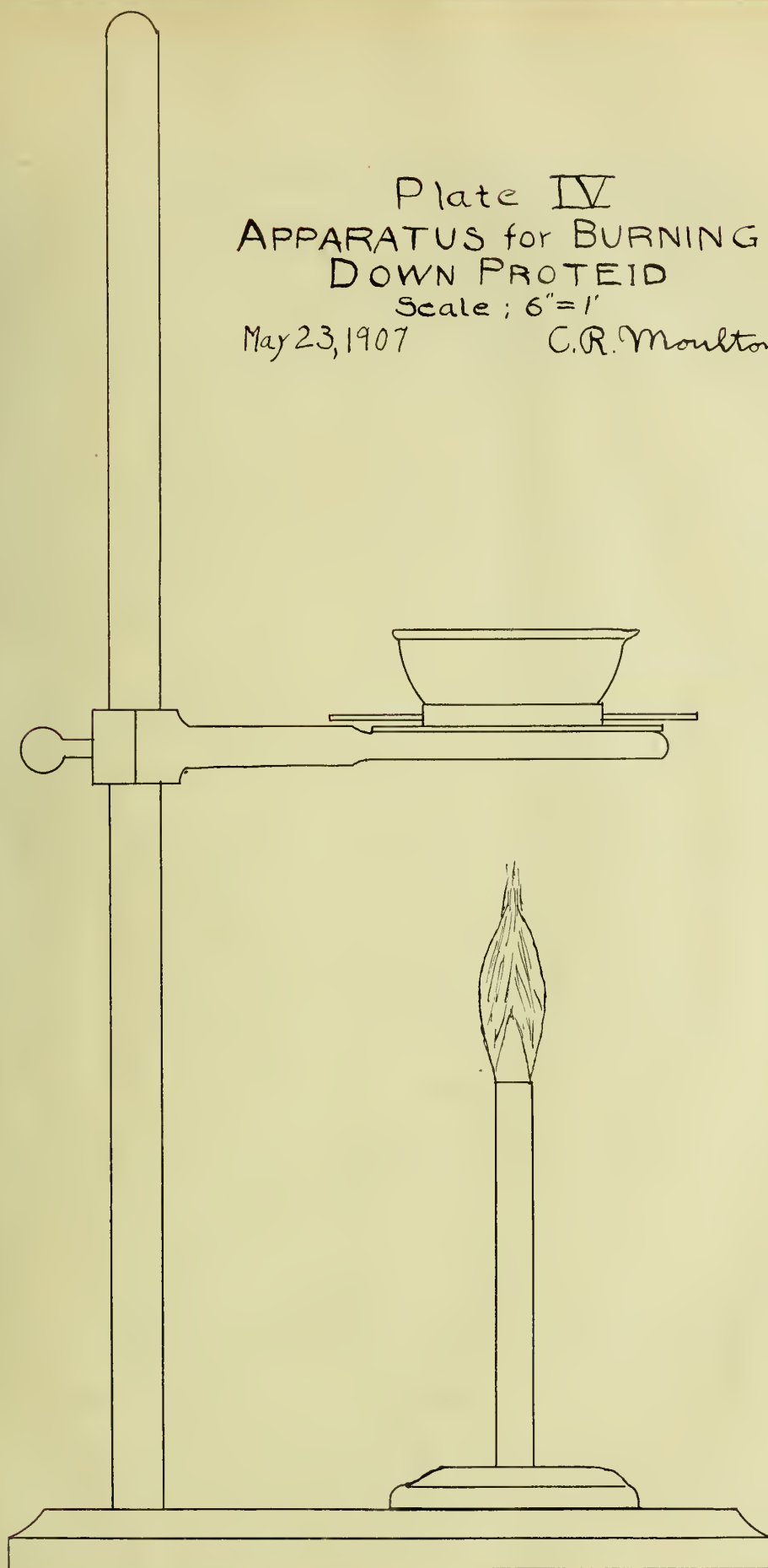ELECTRIC BOMB
Scale: 12" = 1'
May 23, 1907. C.R. Moulton

Plate IV
APPARATUS for BURNING
DOWN PROTEID
Scale ; 6"= 1'
May 23, 1907   C. R. Moulton.

The general object of this thesis was, at first, to
work out a method for the combustion, in large quantities,
of organic material for the estimation of small amounts of
sulphur and phosphorus. But owing to lack of time and other
causes the specific object came to be the working out of a method
for the estimation of phosphorus in coal, coke, and proteid,
the preliminary step being the combustion of large amounts of
the organic material in the peroxide bomb.

The usual methods are elaborate and difficult for
transforming organic material into solutions containing no
organic matter. As examples we have Kjeldahl digestions
and burning down the material to an ash and leaching the ash
with nitric acid. On the other hand it is a very simple and easy
matter to burn one or one-half gram of coal or coke, or other
organic substance, in the peroxide calorimeter. So if we could
increase the capacity of one of these bombs to accomodate
about five grams of organic material with the corresponding
amount of sodium peroxide we would have an easy means of preparing
the substance for analysis. Thus our first object of
investigation was to determine the lowest ratio of chemical
to organic matter and to study the behavior of various mixtures
in the bomb. It was desired to find the mixture which would burn
the greatest amount of carbonaceous or organic matter to the

smallest amount of chemical and to employ a large bomb, if necessary, to make possible the combustion of five grams of material.

For this purpose a special, large, though crude, bomb was made. A cut of this bomb in shown in Plate I. Page 15 It consists of a hollow cylinder of steel whose two end caps are held on by triangular plates bolted together. The nuts on one end of the bolts are easily loosened and the plate and cap removed. The volume of this bomb is about 4.3 cu. in., or twice as great as the standard Parr bomb. After the materials in the bomb had been thoroughly mixed by shaking, it was necessary to support the bomb on a tripod and heat it by a Bunsen flame to cause ignition. The majority of the mixtures used contained boric acid. This makes an easily fusible mass which retains its oxidizing properties.

In the first ten experiments the bomb above described was used and coal was the organic material investigated. Below is a table showing the charges used and the results obtained.

Table 1.

Experiments with Bomb Shown in Plate I.

No.	Coal.	Mixture.		Peroxide.	Result.	Time.
1	1 gr.	0.5 gr.	2 pts. $B(OH)_3$ 1 pt. KNO_3	10 gr.	Good combustion.	3 min.
2	2 gr.	0.5 gr.	2 pts. $B(OH)_3$ 1 pt. KNO_3	10 gr.	Three trials. See below.	3-4 min.
3	2 gr.	1.0 gr.	2 pts. $B(OH)_3$ 1 pt. KNO_3	10 gr.	Poor combustion.	4 min.
4	2 gr.	2.0 gr.	11 pts. $B(OH)3$ 4 pts. $KClO_3$ 1 pt. Mg	10 gr.	Poor combustion	4 min.
5	2 gr.	2.0 gr.	11 pts. $B(OH)3$ 4 pts. $KClO_3$ 1 pt. Mg	20 gr.	Perfect combustion	4 min.
6	3 gr.	2.0 gr.	11 pts. $B(OH)_3$ 4 pts. $KClO_3$ 1 pt. Mg	20 gr.	Explosion	4 min.
7	3 gr.	2.0 gr.	$B(OH)_3$	20 gr.	Poor combustion	4 min.
8	3 gr.	1.5 gr.	2 pt. $B(OH)_3$ 1 pt. KNO_3	20 gr.	Explosion	4 min.
9	3 gr.	None		20 gr.	No combustion	5 min.
10	3 gr.	0.5 gr.	Mg	20 gr.	No combustion	4 min.

No. 1 was very quiet and complete. There was no

pressure noticeable on opening the bomb.

The first trial of No. 2 gave a poor combustion, for the

materials had not been shaken well. In the second trial the
bomb had not been heated long enough to cause ignition. The
third trial resulted in an explosion after heating four
minutes. A channel was torn out of the bomb between the cap
and the end of the cylinder.

In No. 3 coal was left unburned and the acidified
solution gave an odor of H_2S, showing an incomplete combustion.

No. 4 was incomplete for the acidified aqueous
solution gave a strong odor of H_2S and the blue color of a
ferricyanide.

The explosion in No. 6 was probably due to the
reaction's proceeding too rapidly.

In No. 7 the $B(OH)_3$ was added to slow down the
reaction, but a very poor combustion resulted.

No. 9 and No. 10 were repeated twice.

The bomb used in these trials was seen to have
several disadvantages. The heating with an external flame
caused the bomb to be heated well throughout and leaving it
in a poor condition to withstand high pressures. A combustion
caused by general heating is on the order of an explosion, while
when it is caused by concentrated heat at one point it proceeds
quietly. The joint where steel cap met steel cylinder was not
very good even though the two were ground together with emery.

It would probably be better to use a bomb where the joint was
made tighter by a gasket. For the above reasons it was decided
to use a large electrically ignited bomb which had been made
especially for F. W. Gill in his work mentioned above. This
bomb is a large Parr bomb of six cubic inches volume. A cut
of it is shown in Plate II. Page 16.

Table 2.

Experiments with Bomb Shown in Plate II .

No.	Coal.	Na$_2$O$_2$.	Mixture.	Result.
11	2 gr.	10 gr.	1 gr. 4 pts. KNO$_3$: 1 pt. KClO$_3$	Poor combustion
12	2 gr.	10 gr.	1 gr. 4 pts. KNO$_3$. 1 pt. KClO$_3$. 0.5 g. NH$_4$Cl.	Combustion little better
13	2 gr.	10 gr.	1.5 gr. (NH$_4$)$_2$CO$_3$	Poor combustion
14	2 gr.	10 gr.	1.5 gr. NH$_4$Cl	Not as good as 12
15	2 gr.	10 gr.	1 gr. 4 pts. KNO$_3$. 1 pt. KClO$_3$. 1 gr. NH$_4$Cl	Poor combustion

In these five cases the bomb was very large in comparison
with the amount of materials used. It was thought that a small
bomb would keep the material in closer contact and thus insure
a better combustion. Consequently a standard bomb of about
two cubic centimeters capacity was used in trial No. 16
with 2 gr. of coal, 1 gr. of a mixture of 4 pts. KNO$_3$ to 1 part

$KClO_3$, 1 gr. of NH_4Cl, and 10 gr. of sodium peroxide. A big
hole was blown through the side of the bomb near the bottom.

In trials No. 17 and No. 18 the large electric
bomb was used with 3 grams of coal, 1.5 grams of a mixture of
2 parts $B(OH)_3$ to 1 part KNO_3, and 30 grams of peroxide. In
No. 17 the combustion was incomplete and similar results were
obtained to those in trial No. 4, Table I. In No. 18 an
explosion resulted and the bottom of the bomb was blown out.

In the six following tests an old standard bomb
with hot wire ignition was used. The bomb was old and it
did not matter if it were blown up.

Table 3.

Experiments with Old Standard Bomb.

No.	Coal.	Na_2O_2	Mixture.	Result.
19	0.5 gr.	10 gr.	1 gr. 2 pts. $B(OH)_3$. 1 pt. KNO_3 1 pt NH₄Cl.	Very good combustion
20	0.75 gr.	10 gr.	1 gr. 2 pts. $B(OH)_3$. 1 pt. NH_4Cl. 1 pt. KNO_3	Rather incomplete combustion
21	0.5 gr.	10 gr.	0.75 gr. $B(OH)_3$ 2 pts. KNO_3 1 pt.	Good combustion.
22	0.75 gr.	10 gr.	0.75 gr. $B(OH)_3$ 2 pts. KNO_3 1 pt.	Good combustion.
23	1 gr.	10 gr.	0.75 gr. $B(OH)_3$ 2 pts. KNO_3 1 pt.	Incomplete combustion
24	1 gr.	10 gr.	0.5 gr. $B(OH)_3$ 2 pts. KNO_3 1 pt.	Incomplete combustion

In No. 20 the H_2S and ferricyanide were again noted. No. 23 and No. 24 gave results similar to No. 20. Comparing 20, 23, and 24 with trial No. 1, it would seem that in No. 20 the NH4Cl interferred with a good combustion and that in 23 and 24 the method of ignition, the size of the bomb, or the quality of the coal had impaired the completeness of these combustions.

Experiment 25 was performed with the large electric bomb. Two grams of a mixture of 2 pts. $B(OH)_3$ to 1 pt. KNO_3, 2 grs. of coal, and 20 grs. of Na_2O_2 were used, and on ignition a bad explosion resulted.

In the above twenty five experiments all attempts to reduce the ratio of peroxide to coal below ten to one have been failures. Even when this ratio has been employed and more than two grams were ignited in the big bombs the result has been an explosion.

Since the attempt to increase the amount of organic matter that could be burned in a bomb had failed it was decided to try burning the organic matter down to a bulk low enough to suit the requirements of the standard bomb. In the five experiments following five grams of coal were burned down to about one gram and burned in the nickel steel bomb shown in

Plate III. Page 17.

Table IV.

Experiments on Combustion of Ash.

No.	Coal.	Ash.	Na_2O_2	Mixture.	Result.
26	5 gr.	1 gr.	10 gr.	0.5 gr. starch. 1 gr. 11 pts. $B(OH)_3$. 4 pts. $KClO_3$. i pt. Mg.	Some carbon left
27	5 gr.	1 gr.	10 gr.	0.3 gr. sugar. 1 gr. 11 pts. $B(OH)_3$. 4 pts. $KClO_3$. 1 pt. Mg.	Good combustion
28	5 gr.	1 gr.	10 gr.	0.3 gr. sugar. 1 gr. 11 pts. $B(OH)_3$. 4 pts. $KClO_3$. 1 pt. Mg.	Good combustion
29	5 gr.	1 gr.	10 gr.	0.3 gr. sugar. 1911 pts. $B(OH)_3$. 4 pts. $KClO_3$. 1 pt. Mg.	Good combustion
30	5 gr.	1 gr.	10 gr.	0.3 gr. sugar. 1 gr. 11 pts. $B(OH)_3$. 4 pts. $KClO_3$. 1 pt. Mg.	Good combustion

As the ash did not contain sufficient carbon the starch and sugar were added to furnish fuel for the combustion.

In No. 26 the ash had not been ground finely and considerable ash was left in the acidified aqueous solution.

In No. 27 the ash, sugar, and mixture were ground together and then placed in the bomb. There was still some ash left in the solution.

In No. 28 the ash was ground very finely and consequently there was a minimum residue remaining on solution of the cake. No. 29 and No. 30 are the same as No. 28 with practically no

no carbon or ash left but some gritty residues.

The insoluble portions of the above combustions were made soluble by digestion with conc. H_2SO_4 aq. in a platinum crucible. The solutions were then tested and found to contain iron and silicon. The gritty residue is probably nothing but silica colored with Fe_2O_3, the coal furnishing the silica and the fuse wire the iron.

The coal used above was known both by test and by previous analysis to contain no phosphorus. As it was now desired to test the process for its effect on phosphorus analyses, two samples were prepared as in experiments No. 29 and No. 30, and 0.5000 gr. of Kahlbaum's $(NH_4)_2HPO_4$ was added to each ash, the combustion being carried out in the bomb as usual. The aqueous solution from the bomb was acidified with nitric acid and precipitated twice with ammonium molybdate solution as per the method of Way[27]. The analysis was completed as per Pemberton's Titration Method[28] with standard KOH solution.

Table V.

Analysis for Phosphorus in Coal Ash.

No.	Coal.	$(NH_4)_2PO_4$ added.	% P calculated.	% P by analysis.
31	5 gr.	0.5000 gr.	2.345 p.ct.	2.345 p.ct.
32	5 gr.	0.5000 gr.	2.345 p.ct.	2.335 p.ct.

The results here are very good, and they show that
the combustion in the bomb is well adapted as a preparatory
step for phosphorus analyses. But since an inorganic phosphorus
salt was used as the source of phosphorus it leaves a doubt
as to the adaptability of burning down with incineration
an organic substance intended to be analyzed for phosphorus.

In order to determine the effect upon phosphorus
in organic material of burning in an open vessel it was
decided to analyze some proteid for phosphorus by the above
method. The proteid was some prepared from baby beef in the
food research laboratory of the University of Illinois.

Five grams of the proteid were placed in a small
porcelain crucible and burnt to an ash at a low temperature
using a small Bunsen flame and keeping the crucible mostly
covered by the lid during the first half of the operation.
One gram of a mixture of 11 parts $B(OH)_3$ to 4 parts $KClO_3$ to 1
part Mg, 0.3gr sugar, and 10gr Mn_2O_2 were used in the combustions, which were about perfect. The
method of analysis was precisely as in experiments 31 and 32.
The proteid was known to contain about 0.1 per cent phosphorus.

Table VI.

Volumetric Analysis of Proteid for Phosphorus .

No.	Proteid.	Per cent P present.	Per cent P from analysis.
34	5 gr.	0.1%	0.043%
35	5 gr.	0.1%	Lost this
36	5 gr.	0.1%	0.0374%
37	5 gr.	0.1%	0.0447%

In 36 and 37 the proteid was burned down to about
one half gram. There was thus enough carbon left to support
combustion and no sugar was added. The ash was fused in the
bomb without grinding.

Table VII.

Further Volumetric Analysis of Proteid.

No.	Proteid.	Ash.	Mixture.	% P present.	% P by analysis.
38	5 gr.	0.66 gr.	1 pt. $B(OH)_3$	0.1%	0.044%
39	5 gr.	0.60 gr.	1 pt. $KClO_3$	0.1%	Lost this

1 gr

In 38 and 39 one gram of a mixture of $B(OH)_3$ and
$KClO_3$ in equal parts was used and the ash was ground very
finely. On account of the nature of the carbonaceous ash
the magnesium of the previous mixture was not necessary;
so it was omitted here. The combustion in the bomb was much
more complete than in the previous four cases. The method of

analysis was the same.

The analytical results in the six tests just above are very low. To see whether the fault was in the method of analysis, e. g., the volumetric method, two analyses were run in which the phosphorus was determined gravimetrically as $Mg_2P_2O_727$. Precipitation was made twice with ammonium molybdate and once with magnesia mixture.

Table 8.

Gravimetric Analysis of Proteid.

No.	Proteid.	Ash.	Sugar.	Mixture.	% P present.	% P by analysis
40	5 gr.	0.17 gr.	0.3 gr.	1 gr. {1 pt. $KClO_3$	0.1%	0.053%
41	5 gr.	0.20 gr.	0.3 gr.	1 pt. $B(OH)_3$}	0.1%	0.058%

In these two tests 1 gram of a mixture of equal parts of $KClO_3$ and $B(OH)_3$ and 10 gr. of Na_2O_2 were used. The ash was ground as before.

The gravimetric method gives higher results than the titration method. But we can not say that the difference is due solely to the method. If the phosphorus is being volatilized a difference in the intensity of the heat would cause a difference in the analytical results.

Considerable difficulty was attendant upon the above attempts to burn down five grams of proteid in small No. 1 porcelain crucibles. The mass easily became tarry in

consistency and some ash was lost by boiling over and spitting.
In the two following tests large three inch porcelain
crucibles were used, the proteid was burned almost completely
to an ash, and the combustion was carried out with 10 grams
of Na2O$_2$, 0.3 gram sugar,and one gram of a mixture of equal
parts B(OH)$_3$ and KClO$_3$.

Table 9.

Further Gravimetric Analyses of Proteid.

No.	Proteid.	Ash.	Sugar.	Mixture.	% P present.	% P by analysis.
48	5 gr.	0.1 gr.	0.3 gr.	1 gr. 1 pt. KClO$_3$	0.1%	0.0601%
49	5 gr.	0.1 gr.	0.3 gr.	1 pt. B(OH)$_3$	0.1%	0.0656%

These results are somewhat higher, but this may be
due to a slightly different sample of proteid.

In all cases where porcelain ware has been used
above the glaze of the porcelain has been apparently attacked
by the carbonaceous material and a complete removal of the ash
was very difficult. It is likely that some phosphorus is
retained in the damaged glaze. In the two following tests
platinum dishes were used in order to do away with the loss of
phosphorus in the glaze. The proteid was burned to one half gram
and fused in the bomb with 10 grams of Na$_2$O$_2$ and 1 gram of equal

parts $B(OH)_3$ and $KClO_3$. A nitric acid extraction was made of a slight residue left in the platinum dishes and this was added to the solution to be analyzed. Analysis was gravimetric as before.

Table 10.

Further Gravimetric Analyses.

No.	Proteid.	Ash.	Sugar.	Mixture.	% P present.	% P by analysis.
50	5 gr.	0.053 gr.	0.3 gr.	1 pt. $KClO_3$	0.1%	0.0868%
51	5 gr.	0.045 gr.	0.3 gr.	1 pt. $B(OH)_3$	0.1%	0.0846%

1 gr.

These two results would tend to show that some phosphorus was being lost in the glaze of the porcelain crucibles, since the analyses are much higher.

The results giving 0.1% of phosphorus in the proteid had been obtained by analyses carried on in the food research laboratory of the University of Illinois. But results obtained by the same person are more comparable than those obtained by two. Likewise the result of 0.1% may be too high. So independent analyses were run. The method used was the one described by Arthur Donaldson Emmett[29] in his M. A. thesis entitled "A Study of the Phosphorus Content of Flesh." It was used by him for total phosphorus and is one of the standard methods

of the Bureau of Chemistry of the U. S. Department of Agriculture.
A slight modification of the method was used. About five
grams of the sample are weighed in triplicate into Kjeldahl
flasks and 50 c. c. of conc. H_2SO_4 are added. The mixture is
cautiously heated until it becomes well charred when it is
allowed to cool slightly and 5-10 grams of NH_4NO_3 (or K_2SO_4 and
some mercury) are carefully added. The digestion is continued
at a low temperature at first then gradually increased until the
liquid boils. When the mixture does not clear up within
one hour 5 grams more of NH_4NO_3 are added and the digestion
continued. (With the K_2SO_4 and mercury this is unnecessary.)
When the liquid has become colorless the oxidized mass is
transferred with the aid of hot distilled water to beakers.
Care is taken in not using too much water and in keeping
the volume well within 200 c. c. When the solution is cold
it is neutralized with strong ammonia, using litmus paper as an
indicator. The further analysis is carried on as described
on page 30.

Three tests were carried out as per above using
5 grams proteid and 10 grams of K_2SO_4 with neither mercury
nor NH_4NO_3. This was unsatisfactory, for either the large
amount of $KHSO_4$ in the solutions or incomplete breaking up of all
organic matter present caused the failure to get a precipitate.

Four further tests were made as per above using
5 grams proteid, 5 grams K_2SO_4, and some mercury.

Table 11.

Kjeldahl Digestion Standard Analysis of Proteid.

No.	Proteid.	Per cent of P found.
52	5.000 gr.	0.1007%
53	5.000 gr.	0.0857%
54	5.000 gr.	0.0985%
55	5.000 gr.	0.084%

These results are not concordant and some source
of error is evidently to blame. It is a property of this
proteid to absorb moisture very readily. Consequently when
the proteid is weighed out in an aluminium dish, as all the
above have been, the weights will vary greatly owing to the
different amounts of moisture absorbed. In all the following
work the proteid was air dried and weighed by method of
differences from a weighed tube of about twenty five grams
capacity. The proteid was dried in the oven at 105° to 110°
C. until it ceased to lose weight or began to gain a little.
Then the sample was quickly poured out on a large cover glass
and the tube again weighed.

The following are the results of three analyses.

Table 12.

Standard Analysis of Proteid by Kjeldahl Digestion.

No.	Proteid.	$Mg_2P_2O_7$.	Wt. of P.	Per cent of P found.
56	6.3996 gr.	.0254 gr.	.00707 gr.	0.1105%
57	6.6795 gr.	.0264 gr.	.00734 gr.	0.1100%
58	9.7437 gr.	.0325 gr.	.00905 gr.	0.0928%

The digestion and analysis was carried on precisely as in the preceding four analyses. The results are more concordant here, two of them checking almost exactly.

With these last results as the standard six analyses were run by burning the proteid down in platinum dishes and burning the residue, after grinding, in the bomb. The proteid was burned down nearly to an ash as shown in Plate IV, then *Page 18* a free flame was used to finish. Ten grams of Na_2O_2 and 0.3 gram of sugar were used. Following are the results.

Table 13.

Analysis of Proteid.

No.	Proteid.	$Mg_2P_2O_7$/	% of P found.	% P by Kjeldahl digestion.
59	7.9940 gr.	0.0266 gr.	0.0926%	0.11%
60	5.8258 gr.	0.0192 gr.	0.0916%	0.11%
61	8.1914 gr.	0.0283 gr.	0.0961%	0.11%
62	8.0552 gr.	Lost	-----	----
63	6.6298 gr.	0.0211 gr.	0.0886%	0.110 %
64	8.8337 gr.	0.0234	0.0730%	0.11%

In 59-61 the mixture $KClO_3$ to $B(OH)_3$ 1 : 1 was used.
Since chlorides are known to dissolve ammonium phosphomolybdate
a mixture of $B(OH)_3$ and KNO_3 (2 : 1) was used in 62-64.

By this time the platinum dishes had been used with
the proteid about six times and they were beginning to show
in a marked degree the effect that carbon and a phosphate has
on platinum when heated with it. The red hot carbon had been
reducing the phosphate in the proteid and the phosphorus was
alloying with the platinum. This will account for the low
results of analyses 59-67 as compared with those of 56-58.
Consequently the use of platinum dishes was discontinued.

In the three following analyses three-inch porcelain
dishes were used. The burning down was done asin 59-67.
Ten grams of Na_2O_2, 0.3 gram of sugar, and 1 gr. of a mixture
of 2 parts $B(OH)_3$ to 1 part KNO_3 were used. The analysis was
conducted as above.

Table 14.

Proteid Analyses.

No.	Proteid.	$Mg_2P_2O_7$.	% of P found.	True % of P by Kjeldahl.
68	7.2015 gr.	0.0253 gr.	0.0978%	0.11%
69	7.1996 gr.	0.0250 gr.	0.0967%	0.11%
70	7.2017 gr.	Lost	---	----

In 68-70 the porcelain dishes showed signs of being attacked by the proteid when heated. A few trials were now made of various ways of burning down the proteid in order to see if the attacking of the glaze could be prevented.

The apparatus used is shown in Plate IV. A pipestem *Page 18* triangle was placed on an asbestos centered wire gauze on a three inch ring of a ring stand. The porcelain dish containing about 7.03 grams of proteid was set on the triangle. A Bunsen burner regulated to give a two inch flame was placed beneath the wire gauze with four inches between the gauze and the top of the burner. After thirty or forty minutes most of the volatile matter had gone off and a well charred cake was left. This can readily be turned over with a spatula and glass rod. The cooled dish was placed on a piece of glazed paper to catch any particles that might bescattered. The dish was then heated again. After no more fumes were given off the intensity of the flame was increased. In fifteen or twenty minutes more the proteid had been reduced to a cake weighing from one to one and a half grams. The cooled dish was then placed on the glazed paper and the cake broken up and mashed with a spatula and a piece of large glass rod rounded on the end like a pestle. All particles that had dropped onto the paper

were returned to the dish. The heating was then continued. Finally
the triangle and wire gauze were removed and the porcelain
dish was heated with a low flame for about fifteen minutes,
care being taken not to leave the flame long in one place. In
this manner the proteid was burned down to 0.5 or 0.75
gr. The time occupied was about one hour and a half. The
carbonaceous residue was fairly soft and spongy and the
porcelain glaze was entirely unimpaired, only a carbon mirror
remaining which was readily burned off after the removal of the
residue leaving the weight of the porcelain dish exactly the
same as before the process. The residue, after grinding in a
good glass mortar, gave a perfect combustion in the bomb
with 10 gra,s of Na_2O_2 and 1 gram of a mixture of 2 parts
$B(OH)_3$ to 1 part $KClO_3$.

In the three following analyses the method given
just above was used. The analysis was conducted as described
on page 30 excepting that precipitation was made once with
molybdate and twice with magnesia mixture. It was noted that
this gave a much whiter and better looking $Mg_2P_2O_7$ on
ignition.

Table XV.

Proteid Analyses.

No.	Proteid.	Ash.	$Mg_2P_2O_7$.	% of P found.	% of P by Kjeldahl digestion.
74	7.7584 gr.	0.6656 gr.	0.0232 gr.	0.0832%	0.11%
75	6.4206 gr.	0.5793 gr.	0.0180 gr.	0.078%	0.11%
76	6.9562 gr.	0.6337 gr.	0.0195 gr.	0.0780%	0.11%

The results here are no better, in fact even worse, than some previous results. All sources of error have been removed with two exceptions. Either phosphorus is being lost by volatilization, which is very doubtful, or the boric acid is interfering in the analysis.

The residue after burning down as described above is spongy and probably contains some hydrogen. If so, it will act itself as an accelerator, and so none need be used. An experiment was tried in which the ash was combusted with Na_2O_2 alone. Ten grams was found sufficient for 0.5 to 0.6 gram of residue while 15 grams were needed for 0.75 grams of residue.

The six following analyses were run using no accelerator and between 10 and 15 grams Na_2O_2. The samples were burned down and analyzed as in the analyses just above.

Table XVI.

Proteid Analysis by Our Method.

No.	Proteid.	Ash.	$Mg_2P_2O_7$.	% of P found.
78	6.5190 gr.	0.6405 gr.	0.0229 gr.	0.0972%
79	6.1468 gr.	0.7155 gr.	0.0223 gr.	0.1009%
80	6.4134 gr.	0.7526 gr.	0.0227 gr.	0.0985%
81	6.1777 gr.	0.5329 gr.	0.0224 gr.	0.1009%
82	6.9107 gr.	0.4737 gr.	0.0253 gr.	0.1019%
83	6.8704 gr.	0.5245 gr.	0.0248 gr.	0.1005%

These results were so good that it was thought best to repeat the standard analysis of the proteid using the second method of precipitation-- that is, precipitation once with molybdate and twice with magnesia mixture. The difference in percentage could easily be attributed to the difference in purity of the $Mg_2P_2O_7$. In the second case it burned free of carbon easily and became white, while in the first case the $Mg_2P_2O_7$ was badly discolored. The digestion was conducted as described above for the Kjeldahl flask digestions and the analysis was as in the six preceding analyses (78-83).

Table 17.

Standard Proteid Analysis.

No.	Proteid.	$Mg_2P_2O_7$.	Per cent of P found.
84	6.8768 gr.	0.0257 gr.	0.1040%
87	6.0511 gr.	0.0198 gr.	0.0911%
88	6.0138 gr.	0.0232 gr.	0.1074%
89	5.9948 gr.	0.0222 gr.	0.1031

Comparing these results in a table we have the following:

Table 18.

Per cent of P.	Average.
By Kjeldahl Digestion:	
0.0911%#	
0.1034%	
0.1040%	
0.1074%	0.1048%
0.1074%	
By burning and fusing in the bomb:	
0.0972%#	
0.0985%#	
0.1005%	0.1010%
0.1009%	
0.1009%	
0.1019%	

\# These were omitted in calculating the averages.

The difference in percentage between the two methods is 0.0038% or an error of 3.6%. But 3.6% error when dealing with one tenth per cent of a constituent is very small. The results obtained by burning and fusing in the bomb are consistently lower than those obtained by the Kjeldahl digestion, and so we must conclude that the difference is due to the difference in methods. This slight difference in per cent of phosphorus can hardly be explained, however, by saying that some organic phosphorus is being lost by volatilization when burning the proteid. If this were true we should have our lowest result for phosphorus from a sample of proteid which had been burned to the smallest amount of ash. But in 82 we have the highest percentage of phosphorus with the smallest weight of ash and in 78 and 80 the lowest percentage of phosphorus with the greatest weight of ash. (See Table 16.)

It must therefore be concluded that phosphorus in the proteid is not being lost by volatilization. The slightly lower results may be due to the large amount of sodium salts in the solutions analyzed or to some other cause.

The analyses of the solutions in experiments 78 to 89 inclusive were carried out in a precisely identical manner. The results shown in Table 18 are close enough for ordinarily accurate work.

From what has just been said we may conclude that the method as carried out in experiments 78 to 83 is an entirely reliable method for the analysis of phosphorus in proteid and flesh.

CONCLUSIONS.

The combustion of organic material in the Peroxide bomb is an excellent means of preparing the substance for analysis when the constituents to be determined (such as P, S, halogens) are present in such large amounts that one gram of substance is sufficient for the analysis.

But when about five grams or more of the organic substance must be used the method of burning down to one half gram and then fusing in the bomb is well applicable when the constituent to be determined is not volatile when incineration takes place.

It has been shown that an accelerator is not necessary when burning the carbonaceous ash of proteid in the bomb and that when an accelerator is used neither $B(OH)_3$ nor $KClO_3$ (nor a chloride) may be used.

It has been shown that phosphorus in proteid is not volatilized when incineration takes place.

The Kjeldahl digestion method takes from four to six hours to prepare five or six grams of flesh or proteid for analysis. Our method of incineration in a porcelain dish and burning in the bomb requires one hour and a half or two hours of time. Therefore our method saves from three to four and a half hours of time on an analysis.

BIBLIOGRAPHY.

1. Clark, John. Jour. Chem. Soc. Tr. Vol. 63, p. 1079.

2. Clark, John J. S. C. I. Vol. 11, p. 584.

3. Hempel, Walter. Zeit. f. Anorg. Chem. Vol. 3, p. 193.

4. Edinger, Albert. Ber. d. d. Chem. G. Vol. 28, p. 427.
    Zeits. f. Anal. Ch. Vol. 34, p. 362.

5. Berichte d. Breslauer natur gesellsch. Dec., 1893.

6. Archiv. d. Pharmacie. Vol. 232, p. 226.

7. Chemiker Zeitung. 1894. S 2039.

8. Hoehnel, M. and C. Glaser. Arch. Pharm. 232, p. 222.

9. Schuyler, M. C. Chem. Zeit. 120, 1896 (yr.).

10. Parr, S. W. J. A. C. S. Vol. 19, p. 341.

11. Glaser, C. J. A. C. S. Vol. 20, p. 130.

12. Koch, F. C. B. A. Thesis. Uni. of Ill. 1899.

13. Parr, S. W. J. A. C. S. V. 22, p. 646.

14. Parr, S. W. J. A. C. S. V. 24, p. 167.

15. Kofoid, R. N. B. A. Thesis. Uni. of Ill, 1902.

16. Pringsheim, H. H. Berichte, 36, p. 4244.

17. Konek, F. von. Zeit. Angew. Chem. Vol. 17, p. 881.

19. Konek, F. von, and Joehls, Arthur. Zeit. Angew. Chem.,
     Vol. 17, p. 1093.

20. Pringheim, H. H. Zeit. Angew. Chem. Vol. 17, p. 1454.

21. Pringsheim, H. H. Berichte, 37, p. 2155.

22. Pringsheim, H. H. Am. Chem. Jour. Vol. 31, p. 386.

23. Pringsheim, H. H. and James H. Gibson. Berichte, 38, p. 2459.

24. Gill, F. Wm. B. S. Thesis, Uni. of Ill., 1906.

25. Osborne, Thos. B. J. A. C. S. 24, p. 142.

26. Hall, E. B. B. S. Thesis. Uni. of Ill., 1907.

27. Treadwell and Hall. Analytical Chemistry. Vol. II, p. 346.

28. J. A. C. S., 1894, p. 279. Sutton's Volumetric Analysis, p. 324.

29. Emmett, A. D. M. A. Thesis, Uni. of Ill., 1906.